

Supporting Information

Broadband Ce(III)-Sensitized Quantum Cutting in Core–Shell Nanoparticles: Mechanistic Investigation and Photovoltaic Application

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Experimental details

Reagents: $\text{Gd}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Y}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Nd}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), $\text{Yb}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, (99.9%), NaOH , (>98%), NH_4F , (>98%), 1-octadecene (90%), oleic acid (90%), were all purchased from Sigma-Aldrich. Absolute ethanol (99.85%), methyl alcohol (99.99%), and cyclohexane (99.9%) were purchased from VWR International. All chemicals were used as received without further purification.

Synthesis of lanthanide doped core-shell nanoparticles: The lanthanide-doped nanoparticle was synthesized by following our previous co-precipitation protocol.^[1] Firstly, in a typical procedure to the synthesise of core nanoparticle, 4 mL lanthanide acetates in water (0.2 M) solution was added to a 20 mL binary solvent mixture of OA and ODE in a 50 mL flask. The mixture was heated at 150°C for 50 min before cooling down to 45°C. Subsequently, an appropriate amount of methanol solution containing NH_4F and NaOH was added, and the resultant solution was stirred for 90 min. After the methanol was evaporated, the solution was heated to 290°C under argon protection for 1 h and then cooled down to room temperature. The resulting nanoparticles in mixture were precipitated by addition of ethanol, collected by centrifugation at 6000 rpm for 3 min, washed with ethanol and methanol for several times, and finally re-dispersed in 4 mL cyclohexane. The core-shell nanoparticles were synthesized by a layer-by-layer growth protocol by including preformed nanoparticles as seeds in the as-prepared shell precursor solution.

Synthesis of ligand-free nanoparticles: The as-prepared 4 mL nanoparticle in cyclohexane were extracted and re-dispersed in 8 mL 0.1 M HCl solution. The slurry was sonicated at room temperature for 1 h and kept still for overnight in order to remove the surface oleate ligands. After the reaction, the ligand layer was discarded and nanoparticles were collected *via* centrifugation at 14000 rpm for 30 min and re-dispersed in 4 mL deionized water. The washing process was

repeated twice. The powder of ligand-free nanoparticle was obtained by drying in an oven at 60 °C for 24 h.

Fabrication of hybrid c-Si solar cell: The c-Si solar cell was provided by Shanghai Institute of Space Power Supply, Shanghai, China and was cut to around 1 cm² for further use. The powder of nanoparticle was deposited onto the textured surface of the c-Si solar cell to form the hybrid solar cell.

Characterization: XRD analysis were performed on a Bruker AXS D2 phaser with a graphite-monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). TEM measurements were carried out on a JEOL-JEM 2100F transmission electron microscope operating at an acceleration voltage of 200 kV. HAADF-STEM image were recorded on an FEI aberration-corrected Titan G2 80-200 Chemi transmission electron microscope. The luminescence spectra and decay of water dispersion of nanoparticle were acquired by Edinburgh FLSP920 spectrometer equipped with a nitrogen-cooled NIR photomultiplier tube (Hamamatsu R5509-72). Luminescence quantum yield were measured by using a 12 cm diameter integrating sphere from Labsphere. The excitation source was a pulse YAG laser coupled to an OPO EKSPLA NT342 tunable from 210 to 2000 nm with a pulse duration of 5 ns and a frequency of 10 Hz. The detection system was a Symphony CCD camera coupled to a TRIAX 190 monochromator equipped with a diffraction grating with a dispersion of 14.12 nm mm⁻¹. The monochromator and the sphere are coupled through an optical fiber. The whole system was carefully calibrated. First the reflection intensity of an undoped sample was recorded then the reflection and emission of the doped sample was recorded. The absorption of the sample was calculated as the difference between the two reflection spectra and the quantum efficiency was calculated as the ratio between emission and absorption intensities. The current-voltage characteristics of the solar cells were measured by a Keithley 2400 source meter that was

controlled by a customized LabVIEW programme. Real-time data collection was completed simultaneously during the measurement. The scan rate was set at 0.05 V s^{-1} . The illumination was provided by a 254 nm UV lamp (EXC-15.C provided by Vilber Lourmat) at a power density of 7 mW cm^{-2} . All measurements were performed at room temperature.

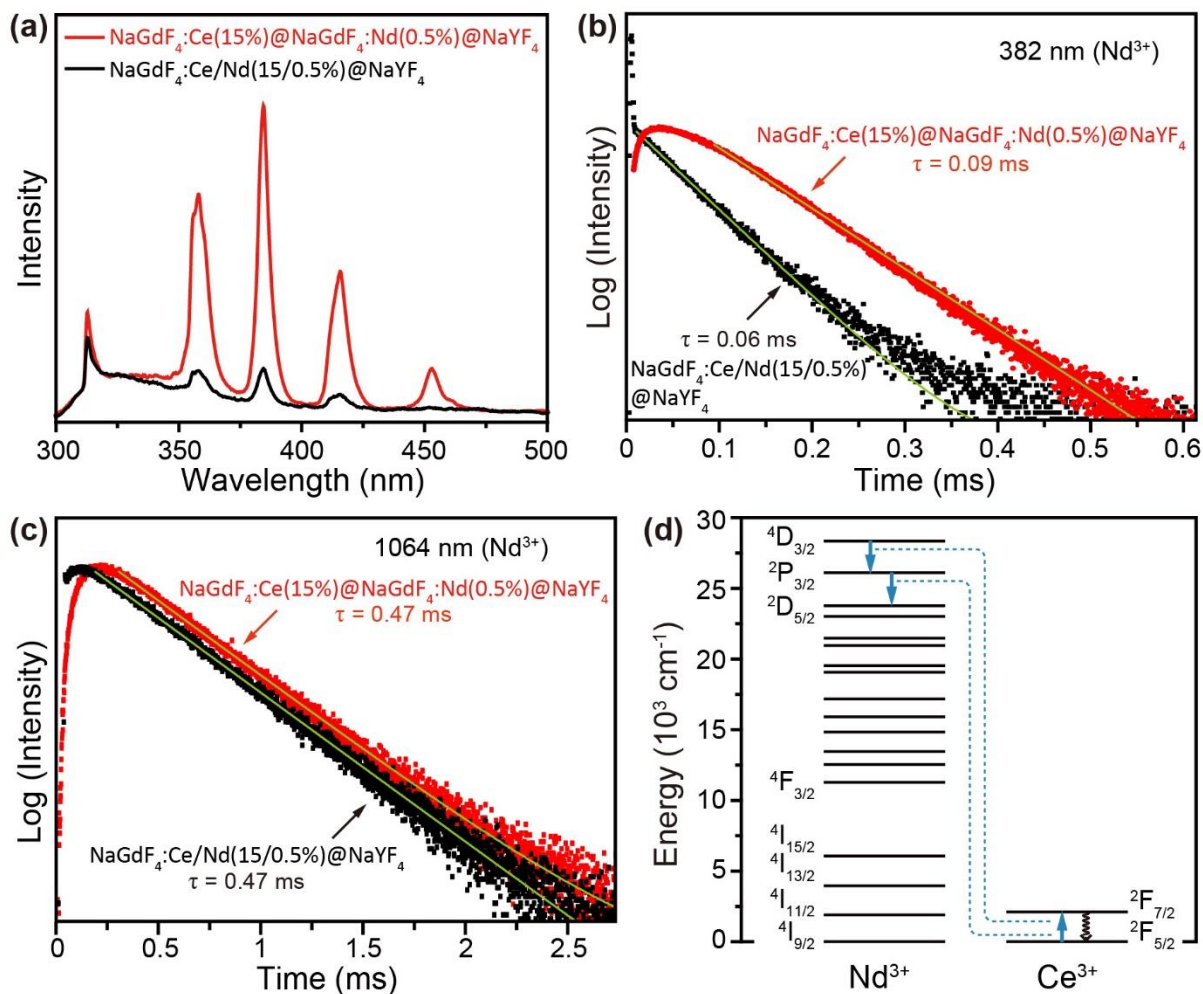


Figure S1. Control experiment demonstrating the necessity of using core-shell nanostructure to sensitize quantum cutting in Nd^{3+} ions with Ce^{3+} . (a) A comparison of emission spectra of $\text{NaGdF}_4:\text{Ce}\text{@NaGdF}_4:\text{Nd}\text{@NaYF}_4$ and $\text{NaGdF}_4:\text{Ce/Nd}\text{@NaYF}_4$ nanoparticles. (b-c) Luminescence decay curves of Nd^{3+} emissions in $\text{NaGdF}_4:\text{Ce}\text{@NaGdF}_4:\text{Nd}\text{@NaYF}_4$ and $\text{NaGdF}_4:\text{Ce/Nd}\text{@NaYF}_4$ nanoparticles at 382 and 1064 nm, respectively. (d) Proposed cross-relaxations between Nd^{3+} and Ce^{3+} that quenches radiative emission from $^4\text{D}_{3/2}$ state of Nd^{3+} .

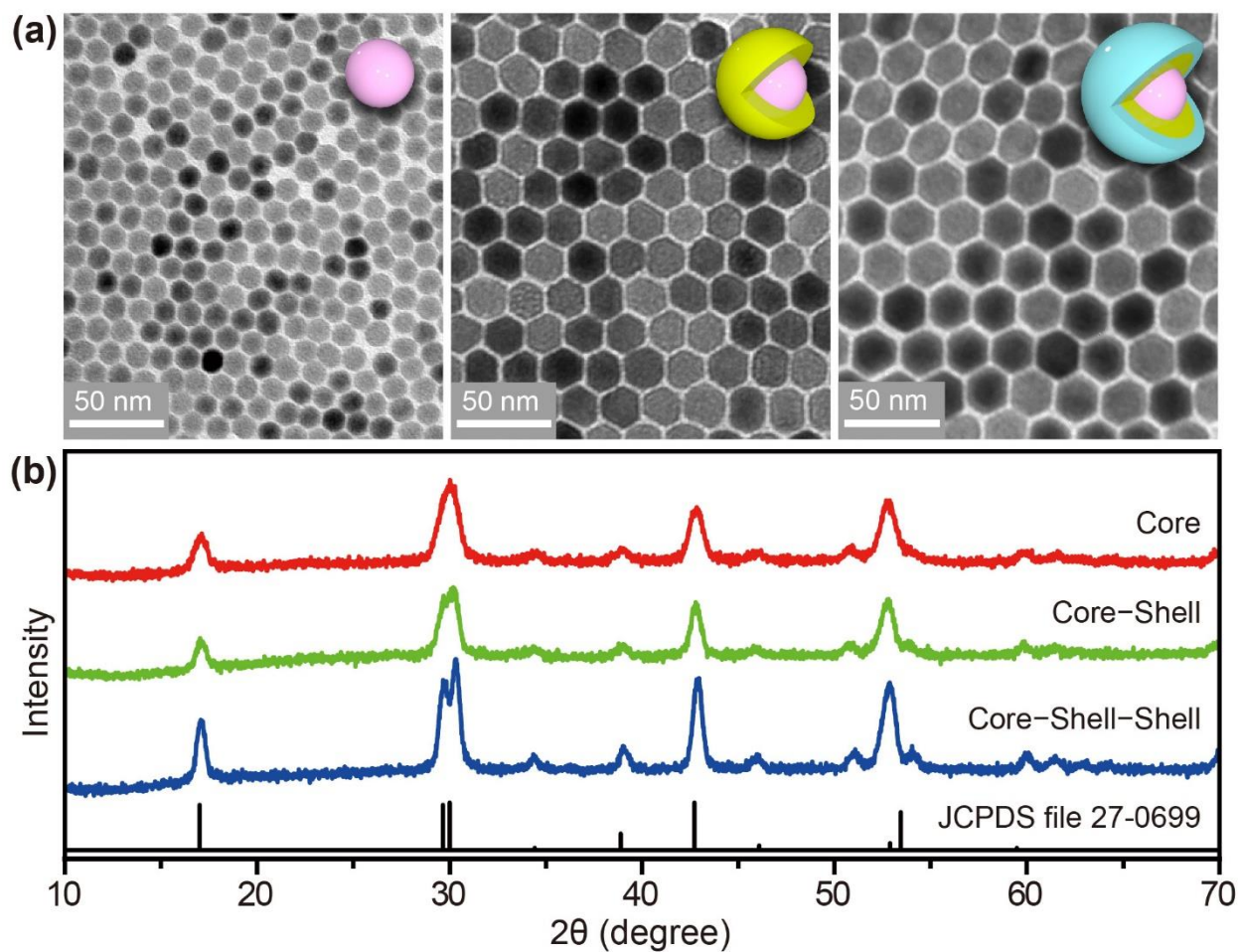


Figure S2. Layer-by-layer growth of the $\text{NaGdF}_4\text{:Ce@NaGdF}_4\text{:Nd@NaYF}_4$ core-shell-shell nanoparticles. (a) TEM images and (b) XRD spectra of the nanoparticles at different stages of the synthesis. The line spectrum in (b) is literature data for hexagonal-phase NaGdF_4 (Joint committee on powder diffraction standards file number: 27-0699).

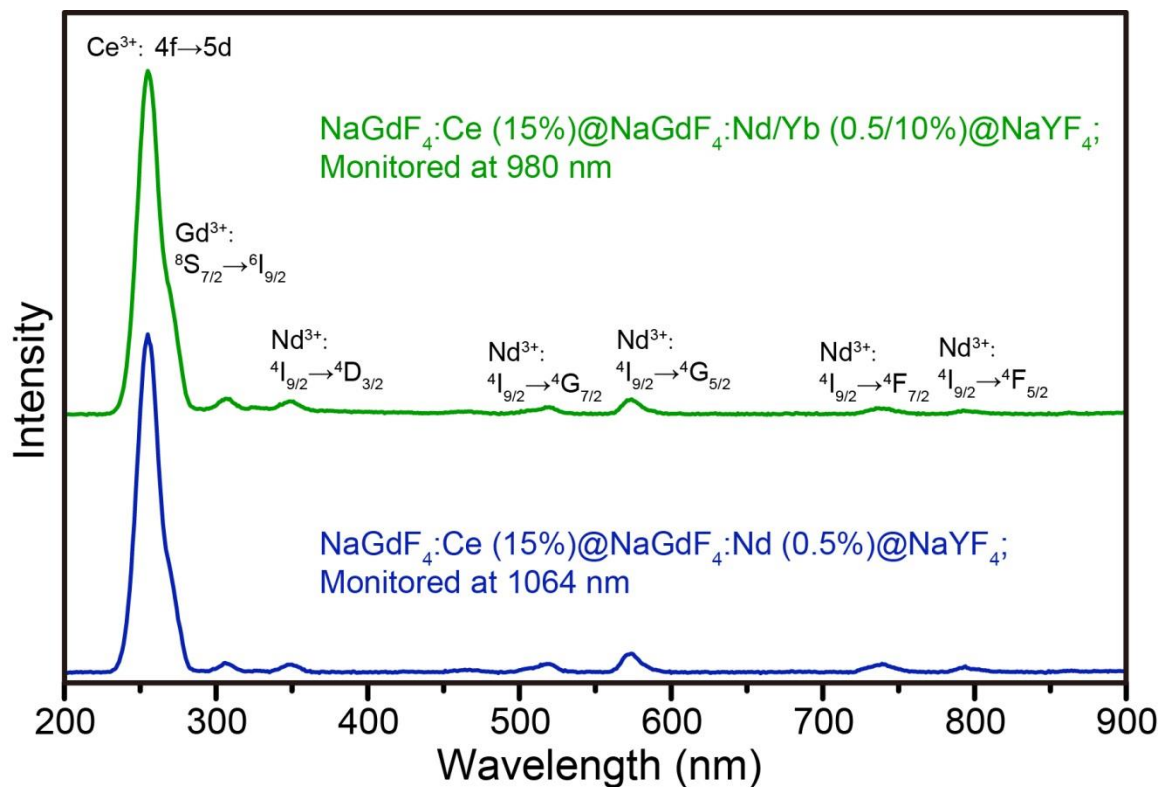


Figure S3. Excitation spectra of NaGdF₄:Ce (15%)@NaGdF₄:Nd (0.5%)@NaYF₄ (monitored at 1064 nm) and NaGdF₄:Ce (15%)@NaGdF₄:Nd/Yb (0.5/10%) (monitored at 980 nm). The spectra are dominated by a broad excitation band due to the $4f \rightarrow 5d$ transition of Ce^{3+} , confirming the effective role of Ce^{3+} in sensitizing the emissions. It is noted that Gd^{3+} transition can also be identified in the excitation spectra. Therefore, Gd^{3+} ions also contribute to the sensitization process, although the role is minor.

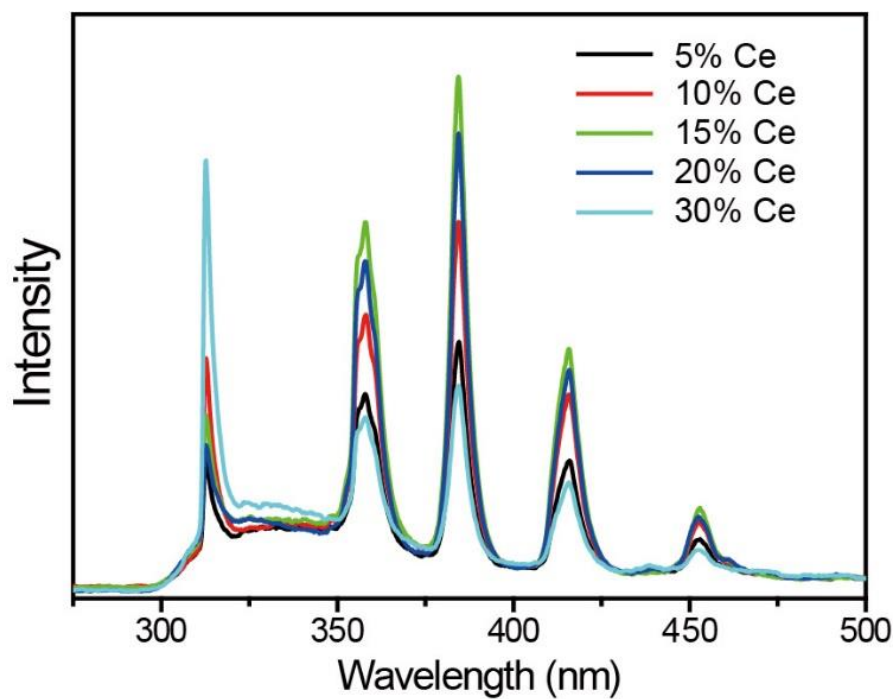


Figure S4. Emission spectra of NaGdF₄:Ce (5-30%)@NaGdF₄:Nd (0.5%)@NaYF₄ nanoparticles as a function of Ce³⁺ dopant concentration in the core layer.

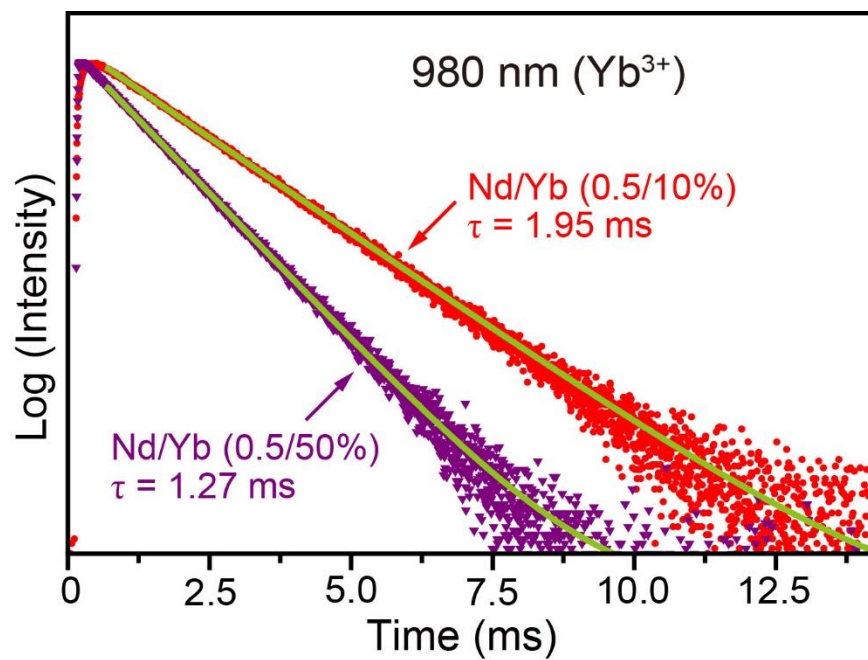


Figure S5. Luminescence decay curves of Yb^{3+} at 980 nm in $\text{NaGdF}_4\text{:Ce (15\%)}@ \text{NaGdF}_4\text{:Nd/Yb (0.5/x\%)}@ \text{NaYF}_4$ nanoparticles as a function of Yb^{3+} dopant concentration.

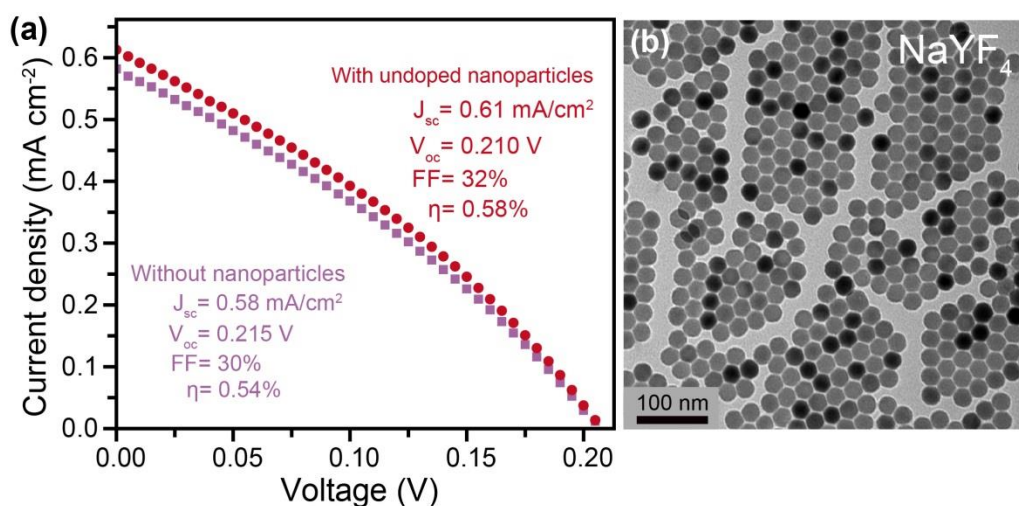


Figure S6. (a) A comparison of current density-voltage characteristic for an uncoated c-Si solar cell and a hybrid c-Si solar cell coated with undoped NaYF_4 nanoparticles. The solar cells were illuminated with a 254 nm UV lamp at a power density of 7 mW cm^{-2} . (b) TEM image of undoped NaYF_4 nanoparticles used in the control experiment. The NaYF_4 nanoparticles display essentially the same size and morphology as the quantum cutting nanoparticles in Figure 1b.

Reference:

- (1) Wang, F.; Deng, R.; Liu, X. Preparation of Core-Shell NaGdF_4 Nanoparticles Doped with Luminescent Lanthanide ions to be Used as Upconversion-Based Probes. *Nat. Protoc.* **2014**, *9*, 1634–1644.